Assignment of Oxidation Numbers
Preliminary Guidelines

There are a number of rules guiding the assignment of oxidation numbers to elements, however, 95+% of the assignments may be made using the following basic rules.

1.) Elements in their standard states are assigned an oxidation number of 0

Examples: $\mathbf{H_2}$ $\mathbf{O_2}$ **Pb** $\mathbf{S_8}$ all have oxidation numbers of 0.

2.) Monatomic ions are assigned an oxidation number equal to the charge on the ion.

Examples: Na^+ Oxidation No. = +1, S^{-2} Oxidation No. = -2 etc.

3.) Elements in Group I, Group II are usually assigned oxidation numbers equal to their common charge.

Examples: $NaClO_3$ - Na is assigned an oxidation number of +1
$KMnO_4$ – K is assigned an oxidation number of +1
$Mg(OH)_2$ – Mg is assigned an oxidation number of +2
CaC_2O_4 – Calcium is assigned an oxidation number of +2

4.) Oxygen in **<u>usually</u>** assigned an oxidation number of -2 in a polyatomic molecule.

The exceptions are O_2, molecules of oxygen alone, such as ozone, O_3^{-1} and peroxides such as hydrogen peroxide, H_2O_2.

Examples: In SO_2, $KMnO_4$ HNO_3, **each** of the oxygens are assigned an oxidation number of -2.

This last one ties everything together in order to allow the assignment of more difficult elements.

5.) The sum of all the oxidation numbers of the elements in a molecule must be equal to the charge on the molecule.

Examples: NaF – From Rule 3.), Na is assigned an oxidation number of +1. The molecule is neutral, therefore, F must be assigned an oxidation number of -1.

SO_3^{-2} – From 4.) oxygen is assigned an oxidation number of -2. Since there are 3 oxygens, each with -2 and the charge on the molecule is -1, Sulfur must have an oxidation number of $x + 3\times(-2) = -1 \quad x = M = +5$

$KMnO_4$ – From 3.), K is assigned an oxidation number of +1 and from From 4.) oxygen is assigned an oxidation number of -2. Since there are 4 oxygens, each with -2 and the charge on the molecule is 0, Mn must have an oxidation number of $(+1) + x + (4\times(-2)) = 0 \quad or \quad x = Mn = +7$

Redox Balancing Method
BLB Method (OOHe)

Discussed in the lecture text by Brown and Lemay, this method, which I call the OOHe method (pronounced oowee!) stands for the order in which the items in the reaction are balanced. In order, the letters mean:

O = Other atoms
O = Oxygen
H = Hydrogen
e = electrons

Consider the reaction**:** $Cr_2O_7^{-2} + H_2C_2O_4 \rightarrow Cr^{+3} + CO_2$

Step 1: Assign oxidation numbers and break up the reaction into an oxidation half reaction and a reduction half reaction.

Ox # +6 → +3

$Cr_2O_7^{-2} \rightarrow Cr^{+3}$ (reduction half reaction)

Ox # +3 → +4

$H_2C_2O_4 \rightarrow CO_2$ (oxidation half reaction)

Step 2: Balance all the other atoms except for oxygen and hydrogen. (<u>O</u> = Other atoms)

$Cr_2O_7^{-2} \rightarrow \mathbf{2}\ Cr^{+3}$

$H_2C_2O_4 \rightarrow \mathbf{2}\ CO_2$

Step 3: Balance oxygen atoms using water (<u>O</u> = Oxygens)

$Cr_2O_7^{-2} \rightarrow 2\ Cr^{+3} + \mathbf{7\ H_2O}$

$H_2C_2O_4 \rightarrow 2\ CO_2$ **Note: Oxygen atoms are already balanced here.**

Step 4: Balance the hydrogen atoms using H^+ ions. (<u>H</u> = Hydrogens)

$\mathbf{14\ H^+} + Cr_2O_7^{-2} \rightarrow 2\ Cr^{+3} + 7\ H_2O$

$H_2C_2O_4 \rightarrow 2\ CO_2 + \mathbf{2\ H^+}$

Step 5: Balance the charges electrons using water (<u>e</u> = Electrons)

$\mathbf{6\ e^-} + 14\ H^+ + Cr_2O_7^{-2} \rightarrow 2\ Cr^{+3} + 7\ H_2O$

$H_2C_2O_4 \rightarrow 2\ CO_2 + 2\ H^+ + \mathbf{2\ e^-}$

Step 6: Recombine equations, multiplying as needed to eliminate the appearance of electrons on either side of the reaction.

Multiply oxalate ($H_2C_2O_4$) equation by 3. Combining yields

$14\ H^{+} + Cr_2O_7^{-2} + \mathbf{3}\ H_2C_2O_4 \rightarrow \mathbf{6}\ CO_2 + \mathbf{6}\ H^{+} + 2\ Cr^{+3} + 7\ H_2O$

or canceling excess hydrogen ions and waters…

$$\mathbf{8\ H^{+} + Cr_2O_7^{-2} + 3\ H_2C_2O_4 \rightarrow 6\ CO_2 + 2\ Cr^{+3} + 7\ H_2O}$$

Step 7 – If necessary for basic solutions.

For basic solutions, add OH^{-}'s on both sides to neutralize **all** the acidic hydrogen ions, turning them into water. In this instance, I need to add 8 for the H^{+} ions **and** 6 for the oxalic acid for a TOTAL of 14 OH^{-}'s.

Executing, I get..

$$\mathbf{14\ H_2O} + \mathbf{Cr_2O_7^{-2}} + 3\ C_2O_4^{-2} \rightarrow 6\ CO_2 + 2\ Cr^{+3} + 7\ H_2O + \mathbf{14\ OH^{-}}$$

Canceling the extra waters give the final result…

$$\mathbf{7\ H_2O + Cr_2O_7^{-2} + 3\ C_2O_4^{-2} \rightarrow 6\ CO_2 + 2\ Cr^{+3} + 14\ OH^{-}}$$